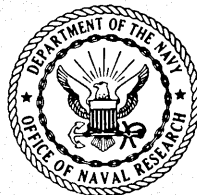


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Abstract: Specific-heat measurements in the 1.2° to 4.2°K range have been carried out on four H-Pd specimens having H/Pd atomic ratios of 0.57, 0.70, 0.81, and 0.88. Corresponding values of γ (the electronic specific-heat coefficient) are 2.52, 1.38, 1.40, and 1.61 millijoules per degree² per gram-atom of palladium; values of Θ_D (the Debye temperature) are 282°, 273°, 276°, and 267°K, respectively. A "dynamic" method of measurement was necessarily employed because of the occurrence of an exothermic process in these alloys. The interpretation of the data was complicated by the interstitial character of these alloys, but the present results for the electronic specific heat appear to offer unusually direct support for the usual simple band picture of Pd and H-Pd alloys. Special care must be exercised in the interpretation of the Debye temperatures in this case.

INTRODUCTION

Although there have been many investigations of the H-Pd system, a satisfactory understanding of its electronic structure has not been achieved. An important problem concerns the disposition of the electrons from the absorbed hydrogen. Although neutron-diffraction measurements (1) on β -phase* alloys at room temperature have shown that the protons from the absorbed hydrogen occupy octahedral interstitial positions of the slightly expanded fcc palladium lattice, the disposition of the electrons cannot be determined by similar measurements and must, in fact, be inferred from other data.

The most pertinent data are those for the magnetic susceptibility (2,3,4) and specific heat (5,6) of Ag-Pd alloys and for the magnetic susceptibility (7,8) of H-Pd alloys. The results of these (and of other somewhat less direct) measurements are usually interpreted on a simple rigid-band model as indicating (a) that pure palladium has roughly 0.6 hole per atom in the d-band and (b) that, in H-Pd alloys, these holes are filled by the electrons from the absorbed hydrogen.

Although the latter view of the nature of H-Pd alloys is of course somewhat oversimplified, it seems basically plausible and has been generally accepted. But the evidence is nevertheless somewhat indirect, since it involves the use of magnetic-susceptibility data, the interpretation of which is complicated not only by the presence of contributions from several sources but also by the difficulty in accounting for exchange and correlation effects. And it may, finally, be mentioned that recent work on the band structure (9) and the de Haas-van Alphen effect (10) in pure palladium seems to indicate that the number of holes per atom in the palladium d-band is substantially smaller than the generally accepted value given above.

Direct and independent information on electronic structure may be obtained from low-temperature heat-capacity measurements, and the results of such work on H-Pd alloys will be reported here.

EXPERIMENTAL DETAILS

The apparatus used in the present investigation has been described elsewhere (11). It may be noted, however, that carbon-resistor thermometry and helium exchange gas were employed. Special procedures were followed in order to remove residual helium gas from the specimen chamber.

Specimens were bulk palladium which had been electrolytically charged with hydrogen. A cylinder

NRL Problem M01-10; Project RR 007-01-46-5408. This is a final report on one phase of the problem; work on other phases is continuing. Manuscript submitted January 20, 1966.

*For H/Pd atomic ratios greater than about 0.6, the H-Pd alloys consist of a single (β) phase. For lower concentrations, the alloys consist of two phases, α and β ; the hydrogen content of the α phase is small, perhaps even zero [see J. Cohen and F. de Bergevin, *Compt. Rend.* **246**:3055 (1958)].

of pure palladium, approximately 1 in. in diameter, 1 in. long, and containing 1.276 gram-atoms, was used for preparing the first specimen. It was initially charged to a concentration well beyond the minimum required to yield an all- β -phase specimen. An unusually extended homogenizing anneal at room temperature was carried out before any heat-capacity measurements were made. This sample was subsequently cut into two cylinders of equal size, and one of these pieces was charged, as appropriate, to the three higher levels of hydrogen concentration. Hydrogen content was determined simply by weighing; the various specimens contained from about 450 to 750 mg of hydrogen. The three specimens of higher hydrogen concentration consisted entirely of β -phase material, whereas the specimen of lowest concentration contained a small amount of α -phase material.

Measurement of the heat capacity could not be made by the usual method of supplying a known amount of energy to a thermally isolated specimen and measuring the resultant temperature change, because these specimens exhibited a spontaneous and continuing temperature rise at all temperatures in the range investigated (1.2° to 4.2°K). It is therefore clear that an exothermic process occurs in H-Pd alloys in the liquid helium temperature range and, it may be added, at both higher (12) and lower (13) temperatures as well. It is of interest to note that this process may consist in the movement of hydrogen from octahedral to tetrahedral interstitial positions, since neutron-diffraction measurements (14) at 4.2°K show that an appreciable fraction of the hydrogen is located at tetrahedral positions, whereas measurements (1) at room temperature show that only octahedral positions are occupied. But, whatever the atomic mechanism, the process* releases energy at a significant rate (typically 1 to 5 microwatts per gram of absorbed hydrogen) and, although this rate decreases noticeably with time, there was no practical possibility of waiting for completion of the process and of then making conventional measurements. Fortunately, values of the heat capacity could

nevertheless be determined by means of a less commonly used "dynamic" method which deals directly with rates of change of specimen temperature.

This alternative method is based on the following simple modification of the basic definition of heat capacity: $C_t = \dot{Q}/\dot{T}$, where C_t is the total heat capacity (of the specimen plus specimen holder), \dot{T} is the rate of change of specimen temperature, and \dot{Q} is the rate at which energy is supplied to the specimen assembly. In the present case, \dot{Q} is the sum of three terms: (a) the known, externally controlled rate, P , at which energy is supplied by a resistance heater attached to the specimen; (b) the unknown rate, H , at which energy is released by the exothermic process; and (c) the unknown, very small, positive or negative, "background" energy transfer per unit time, \dot{q} , arising from radiation, convection, conduction, and vibrational pickup. The quantity \dot{q} will be ignored in the following discussion, since it is essentially negligible and will, under ordinary circumstances, not be separable from H .

The determination of $C_t(T)$ in the present case is necessarily somewhat indirect, since the single basic equation given above involves *two* unknown quantities, C_t and H , in addition to the two easily measured quantities, \dot{T} and P . A further complication arises from the fact that the magnitude of H has been found to vary significantly with time (as was mentioned above) and to depend upon the thermal history of the specimen. The resolution of these problems depends on making one direct and one indirect determination of \dot{T} and P at each given temperature. The measurements must be carried out in such a manner that the values of \dot{T} and H for the indirect determination are *effectively* the same as those for the direct determination; then and only then can the results properly be used to form two simultaneous equations whose solution yields C_t and H .

Specifically, the direct determination simply consists of measuring \dot{T} at a given temperature, for some convenient value of P (typically a few microwatts). And the indirect determination, for which P is conveniently chosen equal to zero, consists in measuring \dot{T} twice, *i.e.*, both before and after the direct measurement, at temperatures $T - \Delta T$ and $T + \Delta T$, respectively. (Typically, $\Delta T \sim 5$ to 40 millidegrees K ; a sequence of three

*The nature and characteristics of the exothermic process will be considered here only insofar as they are relevant to the heat-capacity work; the results obtained by the authors in special investigations of this process will be reported later.

successive measurements of \dot{T} occupies a period of roughly 5 to 10 minutes.) The two values of \dot{T} are then averaged to yield a \dot{T}_{av} . Now a detailed consideration of the properties of C_t and H indicates that, to an entirely adequate degree of approximation for the present work, the quantity \dot{T}_{av} can be "associated" with values of T and H which are equal to those that are applicable to the directly measured \dot{T} . Therefore, the calculation of C_t and H from two simultaneous equations is indeed valid. Previously determined values of the heat capacity of the specimen holder can finally be subtracted from C_t to yield the net heat capacity of the specimen.

Sets of measurements of the above type were made at various temperatures and, in some cases, for significantly different thermal histories, *i.e.*, for significantly different values of H at a given temperature.

RESULTS

Heat-capacity measurements in the 1.2° to 4.2°K range have been carried out on four H-Pd specimens by means of the procedure described above. Several measurements were usually made at each temperature within a comparatively short period of time ($\lesssim 1/2$ hour); the results were averaged before plotting. At least two completely distinct sets of heat-capacity data were taken for each specimen at complementary sets of temperature values. Consistency of the results was good.

Special procedures were followed in some cases in order to obtain distinctly different values of the "spontaneous power," H , at the given temperature. Variations in H by a factor of about two were obtained at some temperatures; within the accuracy of the data, the calculated values of the heat capacity for a given specimen depended only on temperature and not on the rate (H) at which energy was released by the exothermic process.

The heat-capacity data will be presented and analyzed in the following paragraphs. The procedure will differ noticeably from that usually employed, because H-Pd alloys possess several unusual, interrelated characteristics: (a) these alloys are interstitial; (b) the two types of constituent atoms differ greatly in size and environment; (c) the alloy structures are in general not strictly periodic (since $H/Pd < 1$) and, especially

in view of the two previous features, the non-periodicity can hardly be ignored.

One of the most important general results of the present investigation is the following: in the 1.2° to 4.2°K range, a given palladium specimen has a substantially smaller* heat capacity after being charged with hydrogen. This decrease in heat capacity could in principle arise from lattice and/or electronic effects. But the order of magnitude of the observed heat-capacity *reduction* is much larger than the entire lattice contribution to the heat capacity of the palladium specimen at these temperatures. It is therefore clear that lattice effects are of strictly minor importance here and that the present results arise essentially from electronic effects.

Since the electronic heat capacity varies as the first power of the absolute temperature (if there are no unusual interactions), it is now appropriate to emphasize a second feature of the present data, namely, that the temperature dependence of the specific heat of each specimen can be accurately expressed as the sum of a linear term, γT , and a cubic term, bT^3 , the former representing the electronic contribution and the latter representing the lattice contribution to the specific heat. This result is not surprising, but it is also not trivial, in view of the atypical nature of these alloys and in view of the occurrence of a heat-capacity anomaly at higher temperatures. The values of the two coefficients, γ and b , may readily be determined from the intercept and slope, respectively, of the usual C/T vs T^2 plot, where C is the specific heat (Fig. 1 and Table 1). The values of γ and b and their statistical errors (for a 95-percent confidence level) have been calculated for the various specimens by means of a least-squares analysis with a computer. Although separate calculations were made for the two specimens having H/Pd atomic ratios of 0.70 and 0.81, it was not practical to draw two separate lines in Fig. 1.

It is important to note that the specific heat has, in the present case, been defined as the heat capacity of a specimen divided by the number of

*At temperatures in the 30°-300°K range, the heat capacity of a palladium specimen is *increased* by the absorption of hydrogen; and a pronounced peak occurs in the heat capacity curve in the vicinity of 55°K (Ref. 12). These are presumably lattice effects, although the details are not well understood.

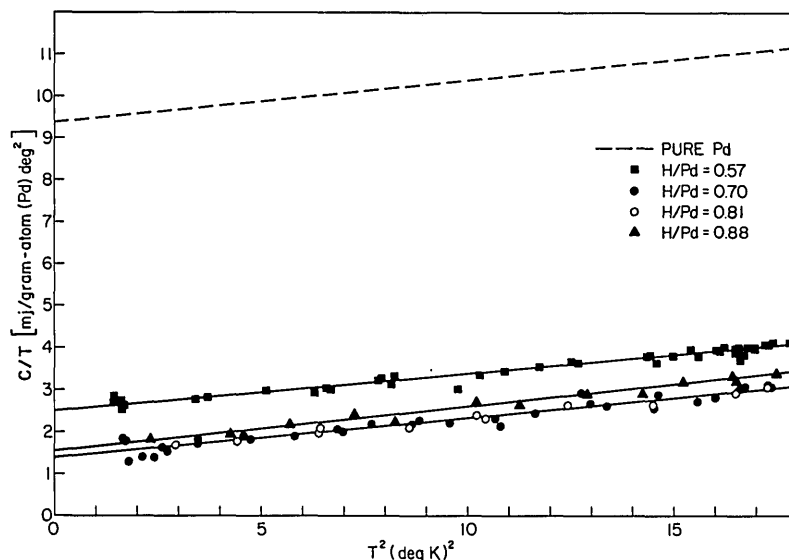


Fig. 1 — Specific heat of H-Pd alloys

TABLE 1
Specific Heat Parameters of H-Pd Alloys

H/Pd Atomic Ratio	Electronic Specific-Heat Coefficient γ (millijoules per degree ² per <i>gram-atom of Pd</i>)	Debye Temperature $\Theta_D(^{\circ}\text{K})$
0.57	2.52 ± 0.06	282 ± 5
0.70	1.38 ± 0.10	273 ± 9
0.81	1.40 ± 0.08	276 ± 7
0.88	1.61 ± 0.13	267 ± 9

gram-atoms of palladium in the specimen, regardless of hydrogen concentration. This choice of specific-heat units may be contrasted with that usually made for substitutional alloys, namely, heat capacity per gram-atom of specimen, or, equivalently, the heat capacity of Avogadro's number of "metal atoms". The latter choice is appropriate for substitutional alloys because in that case the two types of constituent atoms usually have more or less similar sizes and environments; in fact, it is usually assumed that the differences between the two constituents of a substitutional alloy are of secondary importance and produce only minor modifications in the basic electronic structure of the system. But in the present case of H-Pd alloys, there are such large differences in size and environment between the palladium ion-

cores at fcc lattice sites and the hydrogen ions at interstitial positions that it seems physically unreasonable to treat the two constituents as being basically similar. Consequently, it is clearly unsuitable in this case to define the specific heat as the heat capacity of Avogadro's number of "metal atoms," with the difference between H and Pd atoms being ignored for this purpose. The units employed in Fig. 1 are the only practical alternative; as will appear later, these units are indeed useful in analyzing the data.

DISCUSSION

The precise nature of the conclusions to be drawn from the experimental data depends on the viewpoint that is adopted. If no detailed

assumptions are made regarding the electronic structure of H-Pd alloys, then a zero-temperature intercept in Fig. 1, *i.e.*, a γ -value, must be attributed to the specimen as a whole; more specifically, the γ -value will, by means of the usual relation, yield an overall density of states (at the Fermi level) for an *entire* specimen consisting of one gram-atom of palladium and X gram-atoms of hydrogen, where X is the H/Pd atomic ratio. The results of the present investigation may in this context be restated somewhat more explicitly as follows: if a given specimen of pure palladium is charged with hydrogen to a degree corresponding to an H/Pd atomic ratio greater than about 0.6, then the resulting H-Pd specimen will have a total density of states (at the Fermi level) which is equal to roughly 1/6 that of the palladium specimen before charging; and this reduced density of states is roughly independent of composition in at least the $X = 0.70$ to $X = 0.88$ range.

The previous conclusions follow unequivocally from the present experimental results and are of interest for that reason; but they provide little detailed information regarding the electronic structure of H-Pd alloys. A more atomistic interpretation of the data would therefore seem desirable. In this connection, the γ -value for a given alloy may be divided by Avogadro's number (and, of course, by certain other constants as well) to yield a density of states (at the Fermi level) *per palladium atom*.

But such a quantity, obtained for an H-Pd alloy, may be meaningfully compared with the corresponding value for pure palladium *only* insofar as it is reasonable to apportion all of the energy levels (of the specimen) among only the palladium atoms. The latter procedure is in fact open to some question, since the hydrogen ions must be screened by electrons in conduction and/or bound states; such screening might give rise to energy states which cannot properly be associated solely with the palladium atoms. This problem of determining the effect of solute-ion screening on the electronic structure of an alloy arises of course for substitutional alloys, too; in that case, the problem is frequently resolved by means of the rigid-band approximation, which assumes that solute additions change only the degree of filling of the energy bands and not their shape or position. A similar assumption may be made in the present case of interstitial alloys, although

the validity may depend on somewhat different detailed considerations then for substitutional alloys. On this basis, then, the present data may be interpreted as follows: (a) the markedly reduced values of the density of states (at the Fermi level) per palladium atom obtained for the β -phase H-Pd alloys indicate that the electrons from the absorbed hydrogen have entered the unoccupied *d*-states of palladium; (b) the relatively small dependence of γ upon hydrogen concentration indicates that the *d*-band is filled in β -phase H-Pd alloys. Thus, the results of the present investigation may readily be interpreted in terms of the usual simple band picture of Pd and H-Pd alloys and, in terms of that framework, provide unusually direct supporting evidence.

Although the previous conclusions seem reasonable, it should be noted that recent work by other investigators on the band structure (9) and the de Haas-van Alphen effect (10) in pure palladium seems to indicate that there is only about 0.38 hole per palladium atom in the *d*-band—in marked contrast to the generally accepted value of roughly 0.6, which particular value seems to play an important role in the usual interpretation of the nature of Pd and H-Pd alloys. The significance of these new results is not clear; and since the present results do not bear directly on this specific problem, the matter will not be considered further.

Several minor features of the present data will now be considered briefly: (a) the γ -values for the three higher concentration (completely β -phase) alloys do show some concentration dependence; (b) the order of magnitude of γ for these alloys is roughly twice as large as the "noble metal value" that might have been expected for the case of a filled *d*-band (for example, in Ag-Pd alloys (5,6), the value of γ is essentially equal to that of pure silver for all alloys having approximately 60 or more atomic percent silver and, therefore, having a filled *d*-band); (c) the specific heat of the two-phase specimen (H/Pd = 0.57) is distinctly larger than the values obtained for the β -phase specimens.

The first effect is comparatively small and may be simply a matter of a greater filling of the *s*-band or, perhaps, a matter of secondary effects due to changes in the lattice caused by the interstitially located protons. The second effect may be related to one of the problems mentioned in the previous

paragraph. If there were, for example, some energy states which should clearly be associated specifically with the interstitial protons, then the magnitude of a given experimentally determined γ -value should be appropriately reduced before it is used to determine a density-of-states value with which to analyze the electronic structure of the alloy. Such calculations, if appropriate, might yield γ 's more nearly of "noble metal magnitude." The third effect probably arises simply from the fact that the electronic specific heat of a β -phase H-Pd specimen may be substantially increased by the presence of even a small amount of α -phase material, since the latter has a comparatively large electronic specific heat (γ of the α phase may reasonably be taken equal to that of pure palladium). A simple calculation supports the above viewpoint: if the H/Pd atomic ratio in the β -phase region of a two-phase specimen is taken equal to the usual value of about 0.6, and if the values of γ for the coexistent α and β phases are taken equal, respectively, to 9.38 (*i.e.*, the value for pure palladium) and 1.39 (*i.e.*, the average of the values for the 0.70 and 0.81 all- β -phase specimens), then straightforward calculations show that γ should equal 2.8 for a specimen with a H/Pd ratio of 0.57, whereas the present experimental measurements yielded $\gamma = 2.5$. The agreement is thus satisfactory.

Finally, a few comments will be made regarding the information which may be derived from the low-temperature lattice-specific-heat term, bT^3 . The usual treatments of lattice vibrational spectra and specific heats of crystalline solids cannot necessarily be applied here because of the previously mentioned nonperiodicity of these interstitial alloys. Although nonperiodicity occurs of course in substitutional alloys, and in that case is usually completely ignored in regard to lattice effects, there is an obvious and essential distinction between the two cases, namely, that in substitutional alloys the two types of atoms occupy the same set of lattice points, whereas for the present interstitial alloys one type of constituent atom completely occupies a set of lattice points and the other type occupies some fraction of the interstitial positions. No simple, general treatment of latter problems seems to have been made. However, at sufficiently low temperatures, the elastic-continuum treatment of the vibrational modes and of the specific heat will be applicable, in which

case (15) $C(\text{lattice}) = (16\pi^5 k^4 / 5h^3 v^3) T^3$, where C and V are defined, respectively, as the heat capacity and the volume of a specimen containing Avogadro's number of primitive unit cells of the palladium lattice, and where v is the usual weighted average of longitudinal and transverse sound velocities. Since there is precisely one palladium atom per primitive unit cell, these specific heat units are equivalent to those used in Fig. 1 and, therefore, the coefficient b could in principle be interpreted directly and fundamentally in terms of V and v . But suitable data are not available for the velocity of sound in H-Pd alloys.

Alternatively, a more conventional analysis of the coefficient b may be carried out in terms of a Debye temperature, Θ_D , if it is assumed (a) that the vibrational spectrum of H-Pd alloys may be represented in terms of three acoustic branches plus an appropriate number of optical branches, and (b) that the acoustic branches may be represented by means of the usual Debye approximation. In this case (15), $C(\text{lattice}) = (12\pi^4 R / 5\Theta_D^3) T^3$, where C has the units used in Fig. 1 if R is expressed in millijoules per mole-degree. The present data have been used to calculate values of Θ_D , and the results appear in Table 1. It is important to note the precise significance of the calculated Debye temperatures: (a) in the case of the lattice specific heat at liquid helium temperatures, Θ_D may be regarded as merely expressing the coefficient b in a different numerical form; (b) in the case of higher temperatures, however, Θ_D may be substituted into the usual Debye function to obtain the specific-heat contribution of the acoustic modes of vibration—provided that the assumptions discussed above are indeed valid.

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